Electronic Supplementary Material (ESI) for Energy & Environmental Science. This journal is © The Royal Society of Chemistry 2018

# **Supplementary Information**

# Elucidating the Performance and Unexpected Stability of Partially Coated Water-Splitting Silicon Photoanodes

Kiseok Oh,<sup>a</sup> Cristelle Meriadec,<sup>b</sup> Benedikt Lassalle-Kaiser,<sup>c</sup> Vincent Dorcet,<sup>a</sup> Bruno Fabre,<sup>a</sup> Soraya Ababou-Girard,<sup>b</sup> Loic Joanny,<sup>d</sup> Francis Gouttefangeas<sup>d</sup> and Gabriel Loget<sup>\*a</sup>

<sup>a</sup> Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes)-UMR6226, F-35000 Rennes, France.

<sup>b</sup> Univ Rennes, CNRS, IPR (Institut de Physique de Rennes)-UMR6251, F-35000 Rennes, France.

<sup>c</sup> Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, 91192 Gif-sur-Yvette, France.

<sup>d</sup> Univ Rennes, CNRS, ScanMAT-CMEBA – UMS2001, F-35000 Rennes, France.

## **Table of contents**

1. Experimental Section	2
1.1. Reagents	2
1.2. Surface preparation	2
1.3. Electrodeposition	2
1.4. Electrode fabrication	3
1.5. Photoelectrochemical experiments	3
1.6. Surface characterization	5
2. Supplementary figures	7
3. Supplementary tables	23
4. References	

### **1. Experimental Section**

#### 1.1. Reagents

Acetone (MOS electronic grade, Erbatron from Carlo Erba) and anhydrous ethanol (RSE electronic grade, Erbatron from Carlo Erba) were used without further purification. The ultrapure water had a resistivity of 18.2 MΩ cm (Purelab Classic UV). Sulfuric acid (96%, VLSI grade Selectipur) and hydrogen peroxide (30%, VLSI, Sigma-Aldrich) were purchased from BASF and Sigma Aldrich, respectively. NaOH (>98%, ACS reagent) was purchased from Sigma-Aldrich. Boric acid (>99.8%) and NiCl<sub>2</sub>, 6H<sub>2</sub>O (99.3%) were purchased from Alfa aesar.

#### 1.2. Surface preparation

All Teflon vials and tweezers used for cleaning of silicon were previously decontaminated in 3/1 v/v concentrated H<sub>2</sub>SO<sub>4</sub>/30% H<sub>2</sub>O<sub>2</sub> at 105 °C for 30 min, followed by copious rinsing with ultrapure water. *Caution:* the concentrated aqueous H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (piranha) solution is very dangerous, particularly in contact with organic materials, and should be handled extremely carefully. The *n*-type (1-5  $\Omega$  cm resistivity, Phosphorus-doped, double side polished, 275-325  $\mu$ m) (100) silicon wafers were purchased from Siltronix. All the Si surfaces were degreased by sonication in acetone, ethanol, and ultrapure water for 10 min respectively. The surfaces of the wafers were cleaned in piranha solution at 105 °C for 30 min, followed by rinsing with copious amounts of ultrapure water.

#### 1.3. Electrodeposition

Before the electrodeposition of Ni on the *n*-Si wafer, an ohmic contact was prepared as follow: *i*) the oxide layer of clean Si wafer was removed by dipping in a diluted HF solution (5/1 v/v ultrapure water/50% aq. HF) for 2 min. Then, the hydrogenated Si (Si-H) surface was quickly dried by an Ar flow, *ii*) InGa eutectic (99.99%, Alfa Aesar) was applied on the top part of the wafer after scratching with a glass cutter, *iii*) a thin layer of Ag paste (Electron Microscopy Sciences) was painted on the InGa uniformly for covering the InGa contact. After Ag paste dried, the uncoated Si surface was dipped for 2 min in a diluted HF solution (5/1 v/v ultrapure water/50% aq. HF) and quickly dried under an Ar flow. The backside surface was then quickly covered with an hydrophobic adhesive tape (5490, 3M) to prevent electrodeposition on this side. The bare Si-H surface was immersed in the freshly prepared air-equilibrated plating solution that consisted of 20 mM NiCl<sub>2</sub>,6H<sub>2</sub>O and 0.1 M boric acid. The potentiostat used for electrodeposition was a SP 150 (Biologic). The reference electrode was a saturated calomel electrode (SCE, KCI sat.), and the counter electrode was a large platinum plate electrode that was placed in front of the working electrode. The electrodeposition potential was -1.5 V vs SCE that was applied for 5 s (typical chronoamperogramms are shown in Figure S5). After electrodeposition, the coated surface was rinsed with ultrapure water several times and dried with Ar.

#### 1.4. Electrode fabrication

The Ni NPs-coated Si surfaces were further processed to fabricate electrodes. First, the hydrophobic tape that covered the backside was carefully removed, and the electrical contact that was made on the top part for electrodeposition was removed by diamond glass cutter. An ohmic contact was then done on the backside of Si wafer by scratching the surface with a diamond glass cutter; then InGa eutectic was applied on the scratched part and a metal wire, previously inserted into a glass capillary was deposited on the scratched part. A thin silver paste layer was painted to cover the InGa eutectic contact as well as apart of the metal wire. After drying of the paste, epoxy resin (Loctite 9460, Henkel) was deposited to shield the backside and frontside of the surface except an active area comprised between 0.05 and 0.1 cm<sup>2</sup>, the exact geometrical value was measured using the ImageJ software prior to the photoelectrochemical experiments. The electrode was baked in the oven at 90 °C overnight to cure the resin.

#### 1.5. Photoelectrochemical experiments

Cyclic voltammetry (CV), chronoamperometry (CA) and open-circuit potential (OCP) measurements were performed in a three-neck cell comprising a quartz window and gas inlets. The reference and the counter electrodes were an Hg/HgO (1M NaOH) electrode and a Pt cylinder, respectively. The cell was filled with 1 M NaOH (measured pH=13.6) that was constantly stirred and O<sub>2</sub> gas was blown for at least 30 min before the experiments. All electrochemical experiments, including electrochemical impedance measurements and the activation were performed under stirring and in O<sub>2</sub> saturated conditions. The Si surfaces, prepared as previously described, were used as working photoelectrodes. The light was provided by a solar simulator (LS0106, LOT Quantum Design) equipped with an AM 1.5G filter. The power density of the light source, was measured prior to experiments at the position of the photoelectrode using an ILT1400 radiometer (International Light Technologies) to ensure the right power density (100 mW/cm<sup>2</sup>). Electrochemical measurements were performed with a Zennium potentiostat (Zahner). The potentials versus Hg/HgO were converted into potentials versus reversible hydrogen electrode (RHE) using the following relation:

### $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.059 pH = E_{Hg/HgO} + 0.9004$

All reported potentials were intentionally not corrected by the ohmic drop. Unless specified, the CVs and LSVs reported in this work were recorded at 100 mV s<sup>-1</sup> and all potential values reported in the manuscript are versus RHE. The activation of the samples was always performed by applying 100 CV cycles from -0.7 V to 2 V vs Hg/HgO at 100 mV s<sup>-1</sup> under simulated sunlight.

The measurements of faradaic efficiency were performed at constant potential under illumination in a Hoffman cell that comprised a quartz window and two closed graduated cylinders located respectively above the anolyte compartment (that contained the photoelectrode) and the catholyte compartment (that contained the Pt counter electrode).<sup>1</sup> The evolved O<sub>2</sub> gas accumulated in the anolyte headspace, was measured and converted into a number of moles of evolved  $O_2$  gas using the ideal gas law. The theoretical amount of produced  $O_2$  was calculated using the charge delivered by the potentiostat during the electrolysis that was performed for 2h at 2.9 V vs RHE and 3 h at 1.23 V vs RHE.

The Mott-Schottky measurements were performed in the dark by sweeping the potential from positive to negative at 2 kHz and 1 kHz with an AC amplitude of 5 mV and 300 counts per points. The Mott-Schottky equation relates the capacitance to the applied voltage across a semiconductor-electrolyte junction following:

$$\frac{1}{C_{sc}^2} = \frac{2}{eN_{Dopant}2A^2\varepsilon_0\varepsilon_r}(E - E_{fb} - \frac{kT}{e})$$

where,  $\varepsilon_r$  is the relative permittivity of the semiconductor,  $\varepsilon_0$  is permittivity in vacuum, A is the surface area, e is the charge of an electron,  $N_{Dopant}$  is the free carrier density, k is Boltzmann constant, T is the temperature, and E is the applied potential. The x-intercept of the linear region of the MS plot is indicative of the flatband potential  $E_{fb}$ . In order to check the validity of the curves obtained in Figure 2b, we calculated the doping density based on the following relation, obtained by substitution of the Mott-Schottky equation:

$$N_D(cm^{-3}) = \frac{1.2 \times 10^{31} (cm \times F^{-2} \times V^{-1})}{slope (F^{-2} \times cm^4 \times V^{-1})}$$

It led to N<sub>D</sub> values of 5 x10<sup>15</sup> and 1 x10<sup>16</sup> cm<sup>-3</sup> for non-activated and activated photoanodes, respectively, which is in good agreement with the value of resistivity given by the wafer manufacturer (1-5  $\Omega$  cm).

The electrochemical impedance spectroscopy (EIS) was recorded before activation and after activation at 1.23 V vs RHE. The frequency was varied from 120 kHz to 100 mHz with an AC amplitude of 10 mV. The fits shown in Figure 2b were done using the fitting tool of the Thales program (Zahner).

IPCE measurements were performed with a CIMPS-QE IPCE 3 workstation (Zahner) comprising a TLS03 tunable light source controlled by a PP211 potentiostat in the same cell as the one used for classical electrochemical experiments and the applied potential was 1.23 V vs RHE. The light modulation frequency was 1 Hz, the settling time was 10 s and the number of counts 25. The Thales software provided the spectra in photocurrent efficiency (A W<sup>-1</sup>) or in IPCE (%).

In order to check the validity of the IPCE measurements, the IPCE spectra shown in Figure 1c were first converted into photocurrent density (in A W<sup>-1</sup>) spectra as shown in Figure S8a. We then used the AM 1.5G reference solar spectrum obtained from the ASTM (American Society for Testing Materials) webpage (<u>http://rredc.nrel.gov/solar/spectra/am1.5/</u>) in order extract the incident power distribution as a function of the wavelength in the spectral range of our measurements, as shown in Figure S7. Based on these two spectra, the incident power was converted into a photocurrent distribution that was integrated to finally

obtain the value of photocurrent densities under AM 1.5G simulated sunlight at 1.23 V, shown in Figure S8b. The integration of the red spectrum of Figure S8b gives a value of 5 mA cm<sup>-2</sup>, which is in the same range of the reported value  $j_{1.23} = 7.8 \pm 2.4$  mA cm<sup>-2</sup>. The ratio between the integrated value of the red spectrum and the blue spectrum gives a value of 7, which is also in good agreement with the measurements presented in Figure 1b. In addition, the integration the spectrum obtained recorded at 2 V gave a value of 26.5 mA cm<sup>-2</sup>, in good agreement with Figure 1a and 1b.

The applied bias photon-to-current efficiency (ABPE) has been determined as follows:

$$ABPE = \frac{j \times (1.23 - E_{vSRHE})}{P_{in}} \times 100$$

with  $P_{in}$  being the power input (100 mW cm<sup>-2</sup>).

#### 1.6. Surface characterization

Scanning electron microscopy (SEM) was performed using a JSM 7100F (JEOL). SEM picture analysis was performed using the ImageJ software. AFM images were acquired on a NT-MDT Ntegra microscope in semicontact mode with FM tips (resonance frequency around 60 kHz). The images were treated and analysed with the open-source Gwyddion software. The value of NPs diameters were determined by the Gaussian fits of Figure S6, which were based on about 800 values extracted from ImageJ analysis. The values and the confidence intervals of NP heights are the average values and standard deviations, respectively, calculated using 23 (AFM) and 22 (SEM) measurements. XPS measurements were performed with an Mg  $K_{alpha}$  (hv = 1254.6 eV) X-ray source and an Al source (hv = 1486.6 eV) using a VSW HA100 photoelectron spectrometer with a hemispherical photoelectron analyzer, working at an energy pass of 20 eV for survey and resolved spectra. The experimental resolution was 1.0 eV. C1s set at 284.8 eV is used as the energy reference for all the analyses. The samples used for TEM observations were prepared as follow: first Si nanospikes were fabricated following the simple two-step procedure that we recently reported (on the same wafer as for all other experiments),<sup>2</sup> the Ni electrodeposition was performed as described in section 1.3. and these surfaces were processed to fabricate electrodes as described in section 1.4. In case of the activated samples presented in Figure 3f and 3g, the surface were then cycled with 100 CV cycles as indicated in section 1.5. Before TEM observation, a drop of ethanol was applied on the surface, which was then scrubbed with a razor blade in order to detach the nanospikes. A droplet of the so created suspension was applied on a TEM grid that was dried and used for imaging. Transmission electron microscopy (TEM) was performed using a JEOL 2100 LaB<sub>6</sub> microscope operating at 200 kV equipped with a GATAN Orius 200D CCD camera for diffraction and Bright Field (BF) image acquisition and with a GATAN UltraScan 1000 CCD camera for highresolution image acquisition.

X-ray absorption spectra (XAS) were collected at the SAMBA beamline of SOLEIL with a ring energy of 2.75 GeV and a current of 430 mA. The energy was monochromatized by means of a Si 220 double crystal monochromator. The incoming photon intensity was monitored using a N<sub>2</sub>/He-filled ionization chamber and the data were collected as fluorescence spectra using a 36-pixels Ge detector (Canberra) with a 45° outgoing angle. Each sample was measured for about 2 hours, so as to record spectra with a good enough signal/noise ratio. The data collected were normalized to the intensity of the incoming incident energy (measured in an ionization chamber ahead of the interaction point) and processed with the Athena software from the IFEFFIT package. An E<sub>0</sub> value of 8333.8 eV was used for nickel and edge energies were measured considering the first inflection point. Linear combination fittings were carried out using the Athena software on an energy range from 8320 to 8370 eV.

# 2. Supplementary figures



**Figure S1.** SEM pictures showing a *n*-Si surface coated with Ni by electrodeposition at -1.5 V vs SCE during 5 s (before photoelectrochemical activation); a,c,e) top views and b) cross sections. d,f) Binary pictures obtained from c) and e) used by the freeware ImageJ for surface coverage analysis.



**Figure S2.** SEM pictures showing a *n*-Si surface coated with Ni by electrodeposition at -1.5 V vs SCE during 5 s after photoelectrochemical activation; a,c,e) top views and b) cross sections. d,f) Binary pictures obtained from c) and e) used by the freeware ImageJ for surface coverage analysis.



**Figure S3.** a) CVs recorded under AM 1.5G illumination for *n*-Si modified by Ni NPs before (blue) and after (red) electrochemical cycling. CVs recorded in the dark and after electrochemical cycling for *n*-Si modified with Ni NPs (black) and a sputtered Ni thin film (grey). b) Hundred consecutive CVs recorded during the electrochemical conditioning of a *n*-Si surface modified by Ni NPs. All of the curves were recorded in  $O_2$ -saturated stirred 1 M NaOH, at 100 mV s<sup>-1</sup> except for sputtered Ni that was recorded at 20 mV s<sup>-1</sup>.



**Figure S4.** a) CVs recorded for an activated 100 nm-thick sputtered Ni film at 100 mV s<sup>-1</sup> (black) and at 20 mV s<sup>-1</sup> (red). b) Hundred consecutive CVs recorded at 100 mV s<sup>-1</sup> for activating a 100 nm-thick sputtered Ni film. All of the curves were recorded in  $O_2$ -saturated stirred 1 M NaOH.

Figure S4a shows that the scan rate only affects the Ni<sup>III</sup>/Ni<sup>II</sup> redox wave but does not influence OER current density, therefore justifying the use of a scan rate of 20 mV s<sup>-1</sup> in Figure 1a.



Figure S5. Typical chronoamperometry curves obtained for Ni electrodeposition on *n*-Si.



**Figure S6.** Size distribution of the Ni NPs measured before (blue) and after (red) activation, as determined by SEM measurements and ImageJ analyses. *The values of diameter reported in the manuscript corresponds to the central values of the Gaussian fits, the confidence interval corresponds to 0.5 FWHM.* 



**Figure S7.** Irradiance spectrum used for the integration of the IPCE spectrum of Figure 1c, based the AM 1.5G reference solar spectrum obtained from the ASTM (American Society for Testing Materials) webpage (http://rredc.nrel.gov/solar/spectra/am1.5/.



**Figure S8.** a) Photocurrent efficiency spectra obtained for the surface at +1.23 V (thick lines) and +2 V (thin lines) before activation (blue) and after activation (red). b) Photocurrent density spectra derived from the irradiance spectrum of Figure S7 and the photocurrent efficiency spectra of Figure S8a for an as-deposited surface (blue) and the activated surface (red).



**Figure S9.** Plots showing the difference of OER potentials between the sputtered Ni and the *n*-Si-based photoanode as a function of the current density. For the as-deposited surfaces (blue) and the activated surfaces (red).



**Figure S10.** Mott-Schottky measurements performed at 1 kHz for an anode before (blue) and after (red) activation, squares are experimental points and lines are linear fits. Measurements were performed in the dark, in 1 M NaOH saturated with  $O_2$  under stirring.



**Figure S11.** Bode plots obtained for EIS measurements performed at +1.23 V under AM 1.5G illumination in O<sub>2</sub>- saturated 1 M NaOH for *n*-Si photoanodes modified with Ni NPs a) before activation and b) after activation.



**Figure S12.** AFM height profiles used for calculating the average height of Ni NPs present on the surface of *n*-Si after preparation, the AFM pictures are shown in right, together with the corresponding profile lines.



Figure S13. TEM images showing Ni NPs electrodeposited on *n*-Si.



**Figure S14.** TEM images showing Ni NPs electrodeposited on *n*-Si after activation. a,b) Low magnification view showing multiple Ni NPs. c,d) High resolution view showing the external boundary of the NP shell. e,f) High resolution view showing single Ni NPs.



**Figure S15.** a) SAED image of a Si substrate with several Ni<sup>0</sup> NPs. Strong reflections correspond to the Si substrate (italic Miller indexes) and diffractions rings correspond to polycrystalline Ni<sup>0</sup> NPs (straight Miller indexes). b) SAED image of polycrystalline Ni NPs with a polycrystalline shell. *The diffractions rings are discontinuous because of the small number of crystallites in the selected area*. The rings of Ni<sup>0</sup> are indexed in straight characters and the ones indexed by asterisks can be attributed to (starting from the center): *spot 1* (measured 2.64 Å) : Ni(OH)<sub>2</sub> (2.707 Å); *ring 1* (measured 2.39 Å): Ni(OH)<sub>2</sub> (2.33 Å), NiOOH (2.37 Å) and/or NiO (2.41 Å); and *ring 2* (measured 1.53 Å): Ni(OH)<sub>2</sub> (1.48 Å), NiOOH (1.47 Å) and/or NiO (1.476 Å).



**Figure S16.** XPS survey spectra measured on as-deposited (blue) and activated (red) photoanodes, the top spectra were acquired with a Mg source, the bottom spectra were acquired with an Al source.



**Figure S17.** SEM pictures showing a low magnification (a) and a high magnification (b) top views of the surface of a photoanode after photoelectrolysis at +1.23 V for 20 h.



**Figure S18.** LSVs recorded under illumination at the time indicated by dashed lines plotted on the red curve of Figure 7a. The measurements were recorded in O<sub>2</sub>-saturated stirred 1 M NaOH.



**Figure S19.** SEM pictures showing top views of activated photoanodes after being immersed in 1 M NaOH for 30 h under illumination.



**Figure S20.** LSVs recorded under illumination at the time indicated by dashed lines plotted on the blue curve of Figure 7a. The measurements were recorded in  $O_2$ -saturated stirred 1 M NaOH.



**Figure S21.** SEM pictures showing an activated photoanode after the OCP measurements shown in the black curve of Figure 7a, performed in 1 M NaOH in the dark for 6 h.



Figure S22. SEM pictures of an activated photoanode after 15 h at the OCP under illumination in 1 M NaOH.



**Figure S23.** SEM pictures of an activated photoanode before (a) and after being exposed 15 h in the electrolyte under illumination (b). The right parts correspond to respective binary pictures used for diameter measurements.



**Figure S24.** Cyclic voltammetry curves showing the activation of a Ni-decorated *n*-Si photoanode in  $O_2$  saturated 1 M NaOH. The 100 consecutive scans are shown in dark grey, the first scan is in blue and the last scan is in red. *In this case, a graphite rod was used as counter electrode, these results demonstrate that the activation phenomenon is independent of the counter electrode material.* 

## 3. Supplementary tables

**Tables S1.** Tables showing the XANES linear combination fittings performed with the Athena Software. Top table: as deposited, bottom table: after activation. The values for each component are indicated in percentages. "R" is the goodness of fit and "r- $\chi^{2}$ " is the reduced  $\chi^{2}$ .

## As deposited

Fit no.	Ni <sup>0</sup>	NiO	Ni(OH)₂	β-ΝίΟΟΗ	γ-ΝίΟΟΗ	R (%)	r-χ²
1	93	7	-	-	-	0.06	9
2	92	-	8	-	-	0.07	11
3	92	-	-	8	-	0.13	21
4	96	-	-	-	4	0.25	40

## After activation

Fit no.	Ni <sup>o</sup>	NiO	Ni(OH) <sub>2</sub>	β-ΝίΟΟΗ	γ-ΝίΟΟΗ	R (%)	r-χ²
1	70	30	-	-	-	0.28	53
2	66	-	34	-	-	0.32	61
3	60	-	-	40	-	0.31	59
4	70	-	-	-	30	1.7	320
5	60	-	17	22	-	0.17	32
6	60	-	29	-	11	0.17	32
7	64	16	-	20	-	0.10	19
8	60	24	-	-	12	0.09	17

**Table S2.** Values of resistance (R) and capacitance (C), obtained by fitting the experimental values reported in the Nyquist Plot shown in Figure 2b, the equivalent circuit is presented in the inset of Figure 2a.

	Rs	C1 (µF)	R1 (Ω)	C2 (nF)	R2 (Ω)
before activation	119.1	3.0	487.7	28.9	134.7
after activation	105.2	18.7	153.7	18.7	150.4

Table S3. Table showing the effect caused by the type of Si and the Ni coverage on the stability time.

<i>n-</i> Si type	Ni morphology	Stability time (h)
(100)	Dispersed NPs	11
(111)	Dispersed NPs	13
(100)	Film	40 <sup>a</sup>

<sup>*a*</sup>: value taken from reference 3

## 4. References

- 1 G. Loget, J. Padilha, E. Martini, M. Desouza and R. Desouza, *Int. J. Hydrogen Energy*, 2009, **34**, 84–90.
- 2 G. Loget, A. Vacher, B. Fabre, F. Gouttefangeas, L. Joanny and V. Dorcet, *Mater. Chem. Front.*, 2017, **1**, 1881–1887.
- G. Loget, B. Fabre, S. Fryars, C. Mériadec and S. Ababou-Girard, ACS Energy Lett., 2017, 2, 569–573.